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**CORROSION BY KRAFT PULPING LIQUORS**

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# CORROSION BY KRAFT PULPING LIQUORS

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## I. INTRODUCTION

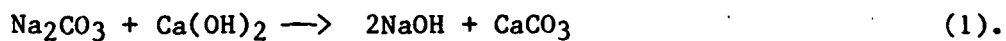
The kraft process is the predominant pulping process used in North America to extract fibers from wood for use in manufacture of paper, tissue, and board. "Kraft" is derived from the German word for "strong," which reflects the high strength of paper products derived from kraft pulp. This high strength, together with effective methods of recovery of pulping chemicals, explains the popularity of kraft pulping. In 1984, more than three-fourths of the pulp produced in the United States — approximately 43,000,000 tons — was manufactured by the kraft process (1).

In the kraft process, hot alkaline sulfide liquor is used to dissolve the lignin from wood chips and separate individual wood fibers for use in paper-making (2). Wood chips are exposed to cooking liquors for several hours at elevated temperature and pressure in a process called digestion. Digestion may occur by repetitive batch processes in small batch digesters, or the process may occur continuously in larger continuous digesters. The contents of the digester are then discharged under pressure into a receiver called a blow tank. Finally, the fibers are separated from the spent liquor in a series of washing stages.

Pulping chemicals are recovered from the spent liquor in a series of process steps shown schematically in Figure 1. First, the spent liquor (known as black liquor) extracted from the pulp is concentrated to 60 percent solids content in multiple-effect evaporators. A soapy by-product called tall oil is

usually extracted from the liquor at some stage of the concentration process. The heavy black liquor is burned as fuel in a chemical recovery boiler. During combustion, the organic constituents of black liquor react exothermically with air to produce steam for process use and for power generation. The inorganic constituents in the spent liquor fall to the bottom of the recovery boiler where they are extracted as a molten salt called smelt.

The smelt recovered from the boiler is converted into cooking liquor in a process known as recausticizing. The molten smelt, which consists primarily of sodium carbonate and sodium sulfide, is dissolved in water to make green liquor. The green liquor is first clarified to remove insoluble dregs and then causticized by exposure to slaked lime. In causticizing, sodium carbonate is converted to sodium hydroxide via the reaction



The calcium carbonate precipitate is removed from the liquor by clarification or filtration, leaving a white liquor with approximately 100 g/L of sodium hydroxide, 30 g/L of sodium sulfide, and lesser amounts of residual carbonates and sulfoxy compounds. The white liquor is stored for reuse as cooking liquor. Meanwhile, the calcium carbonate precipitate (lime mud) is washed and converted to lime in a lime-burning kiln. This lime is later slaked and reused in the causticizing processes.

Although some details vary from mill to mill, the process equipment used in kraft pulping is more or less the same throughout the industry. The principal items include pressure vessels for batch or continuous digestion, rotary drum pulp washers, multiple-effect liquor evaporators, storage tanks for various liquors, chemical recovery boilers, electrostatic precipitators, rotary lime

kilns, slakers, green and white liquor clarifiers, and liquor storage tanks. Ancillary equipment includes pumps, valves, piping, heat exchangers, control instrumentation, and equipment for tall oil processing. To some extent, diffusion washers are replacing rotary drum washers and pressure filters are replacing clarifiers in the modern pulp mill.

Much of the equipment used in the kraft pulp mill is fabricated from plain carbon steel, even though carbon steel has limited resistance to corrosion and cracking when exposed to kraft process liquors. In critical locations (e.g., evaporator tubes in high temperature evaporator effects), stainless steel is routinely used because of rapid attack of plain carbon steel. In other locations, stainless steel may be used to avoid the inconvenience of periodic replacement of carbon steel equipment. In general, the high temperatures and alkalinity of kraft liquors prevent the use of polymeric materials of construction in pulp mill equipment. However, brick and tile linings, as well as sprayed-on concrete linings, are often found in recausticizing equipment, particularly where abrasion is a concern.

Periodically, pulp mill equipment is acid cleaned by recirculation of inhibited acid — usually hydrochloric acid — to remove carbonate deposits that build up on screens and heat exchanger surfaces.

## II. CORROSION IN PULP MILL EQUIPMENT

Batch Digesters. At first, batch digesters were thought to be immune from the severe corrosion affecting digesters used in the sulfite pulping process. In 1930, a catastrophic digester failure killed several workers and prompted the industry to measure the wall thickness of kraft digesters (3). Following subsequent inspections of other digesters, several were retired because of

corrosion-induced wastage of the vessel wall. Thereafter, the industry was vigilant in monitoring the thickness of batch digester walls and retiring vessels that had corroded beyond safe limits.

Corrosion damage appears in batch digesters in several forms, including uniform wastage, large gouges, pitting, and occasional cracking (4). In some cases, the gouges are clearly associated with erosion, either by steam impingement during direct steam heating of the digester, by recirculating liquors, or by impingement of high velocity pulp slurries discharged at the end of a cook. Figure 2 shows an example of erosion-corrosion of a blow target plate used to break the momentum of the pulp mass discharged from the digester under pressure. Grooves are often found beneath blind nozzles and other areas where liquor-saturated pulp can lodge, allowing liquor to run down the walls between cooks. Corrosion is often more severe in the bottom cone area where flow rates are higher during indirect heating and during blows. In some digesters, corrosion is most severe in the splash zone where cooking liquor splashes on the hot sidewalls during digester charging. Welds are often sites of preferential attack in batch digesters, including accelerated corrosion and occasional episodes of stress corrosion cracking.

In the late 1940's, the industry became alarmed over an abrupt decrease in the service lifetime of batch digester vessels because of corrosion-induced loss of wall thickness. At one mill with 20 digesters in operation, the lifetime of digesters installed after 1947 was only 3-5 years, compared with 12-14 years for digesters installed before 1947 (5). Several events apparently combined to increase the corrosion rate. Modern, low-odor recovery boilers introduced about that time were more effective in retaining sulfur in the process, with resultant increases in the sulfidity of cooking liquor. Batch digester production was raised by utilizing more frequent batch cooks of greater severity. Furthermore,

semikilled steel was used to fabricate digesters, replacing the rimmed Bessemer steels used in earlier generations of digesters. Each of these factors played a role in the apparent increase in digester wall corrosion.

Considerable progress was made in understanding and controlling batch digester corrosion as a result of intensive investigations completed in the early 1950's. The effect of liquor composition was thoroughly investigated through surveys and laboratory corrosion studies. General wastage was greatly accelerated by thiosulfates and low concentrations of polysulfides in the cooking liquor (6-7), and by the introduction of air into the digester during charging (8). Linear regression equations (e.g., Eqn. 2) were developed to

$$\text{Corrosiveness} = 3.6 + 0.03 [\text{Na}_2\text{S}] + 0.11 [\text{NaOH}] + 0.04 [\text{Na}_2\text{S}] [\text{Na}_2\text{S}_2\text{O}_3] \quad (2)$$

relate the corrosion rate to concentrations of various minor and major constituents in white liquor (8-9). Laboratory and field studies (10-11) showed that most digester corrosion occurred at the start of the batch cook, and corrosion rates were described in the arcane units, mils per two-thousand cooks (MTTC). Digester walls were found to be passivated during later stages of the cook and reactivated when raw liquor was introduced into the vessel for the next cook. Particularly troublesome was a phenomenon called "hot plate boiling" (12), where liquor charged into the vessel splashed off the chip pile onto sidewalls that were still hot from the previous cook. The evaporative concentration of dissolved chemicals, together with the damage to the passive film from the thermal shock, combined to reactivate the surface of the vessel for further corrosion during the early stages of the next cook.

The influence of the composition and microstructure of digester steel on susceptibility to corrosion remains controversial. von Essen (13) first noted

that steels which were deoxygenated with silicon corroded more rapidly during contact with cooking liquor, relative to steels with lower silicon and higher oxygen levels. This observation explains the preferential attack of high silicon welds that is frequently noted. Several laboratory studies confirmed the effect of silicon on the corrosion rate of steels (14-16), while other studies dismissed the effect as insignificant (17). A similar controversy regarding the benefits of normalizing heat treatments also developed (8,18). The issue of silicon content has never been fully resolved, but many digesters were subsequently fabricated using special "digester" steel (e.g., A285 GrC, containing no more than 0.03 w % silicon) and low silicon weld filler metal (e.g., E6010) in final passes on structural welds.

Digester lifetimes were extended by a variety of measures involving mill operations, the use of linings, and the specification of low-silicon steels. Chip- and liquor-charging practices were modified to eliminate hot plate boiling — e.g., by introducing cooking liquor from the bottom of the digester, using special liquor injection nozzles, and by simultaneous charging of chips and liquor. Graphite brick linings were once used extensively, but stainless weld overlays and thermal-sprayed coatings are now preferred.

The durability of stainless weld overlays has often been inadequate, in spite of promulgation of a TAPPI standard (19) for acceptable overlay practice. Pitting, cracking, and interpass corrosion are the most common complaints. Excessive dilution of the filler metal and production of partially martensitic overlays have been implicated in the poor performance of overlays. The choices of filler metal composition, heat input, and travel speed affect the uniformity of the overlay and the dilution of the filler metal. The TAPPI specification for as-deposited overlay is shown in Table 1. The Schaeffler Diagram predicts that



overlays of the minimax composition will be devoid of the ferrite required to prevent hot cracking. Furthermore, the high allowable carbon concentration may result in sensitization of the overlay by the heat of subsequent weld passes. Consequently, mills often may specify a higher chromium equivalent and lower carbon in the as-deposited overlay.

Blow Target Plates. Erosion-corrosion of the target plate in blow tanks is a continuing maintenance problem, but some advantage can be obtained by using exotic alloys. For example, Hastelloy® C276, a Ni-Cr-Mo alloy, has endured for four years in target plate service where 18-8 stainless steels were lasting for only a few months.

Piping and Ancillary Equipment. Carbon steel piping is subject to corrosion and erosion-corrosion in the kraft pulp mill, but is often chosen for economy. Elbows in blow lines and other areas of high abrasion are particularly susceptible to attack. Type 304L stainless steel is effective in controlling corrosion damage in piping. Pump impellers, pump casings, and valves made from cast CF-8M are usually resistant to attack by kraft liquors.

Continuous Digesters. In contrast to the cyclic environments encountered in batch digesters, wetted surfaces in continuous digesters experience the same environment for months at a time, although the exact environment depends on the elevation in the digester. Wood chips are added at the top of the vessel and the pulp mass works its way downward while the chips are successively saturated with liquor, cooked, washed, cooled, and discharged from the bottom of the vessel. Cooking, extraction, and wash liquors are circulated through the pulp through a series of internal screens and downcomer pipes.

Although the rate of uniform wastage in continuous digesters is usually quite low, on the order of 5 to 10 mils per year, higher rates of attack have been observed locally. In particular, gouging can be a problem where fresh cooking liquor impinges on steel surfaces near the top of the digester. Pitting and washing of welds have also been observed in continuous digesters, but this attack may be a result of acid cleaning practices, rather than attack by cooking liquor.

A severe corrosion problem in continuous digesters literally burst upon the scene in 1980, with the catastrophic failure of a large continuous digester vessel during routine operation (20). The digester ruptured near the top of the vessel because of extensive stress corrosion cracking of shell girth welds. This subcritical cracking was restricted to the welds in the impregnation zone at the top of the digester. Caustic stress corrosion cracking was implicated because of the branched, intergranular appearance of the cracks and the presence of sodium hydroxide in the hot cooking liquor.

Subsequent inspections of similar digesters revealed that more than half of the 140 continuous digesters operating in North America exhibited cracking in structural welds (21). Cracking has been found in girth and vertical shell welds, attachment welds inside the digester, and nozzle welds. Both longitudinal and transverse cracking have been observed, but the deepest cracking has been found in longitudinal cracks in the weld heat-affected zone. Examples of cracking in actual digester welds are shown in Figures 3 and 4.

Most of the cracking has been found in the impregnation zone, where the caustic concentration in the cooking liquor is highest. Furthermore, the residual stresses in impregnation zone welds were often not relieved by post-weld

heat treatment, since the shell is thinner in this zone and stress relief is not required under provisions of the ASME Boiler and Pressure Vessel Code.

An extensive survey of digester cracking statistics failed to reveal differences in digester design or operation that would account for differences in cracking susceptibility (21). As shown in Figure 5, post-weld heat treatment significantly reduced, but did not eliminate, susceptibility to severe cracking.

Cracking similar to digester cracking was reproduced in the laboratory using accelerated slow strain rate and fracture mechanics tests (22). These tests indicated that the caustic concentration in cooking liquors at the impregnation zone was sufficient for caustic cracking of pressure vessel weldments. Furthermore, caustic cracking only occurred when the potential of the digester steel was within a 100 mV range centered close to digester potentials. Figure 6 shows the dependence of cracking susceptibility on potential as determined in slow strain rate tests performed on welded specimens in simulated impregnation zone liquor (23). Potential measurements made on an operating digester indicated that the digester rest potential remained above the cracking range, except for a few days following an upset in operating routine (24).

Two measures have been successful in controlling digester cracking — high alloy barrier coatings placed over susceptible welds and anodic protection. Other remedial measures, such as shot peening, temper-bead weld repair, in-situ stress relief, and unsealed thermal spray coatings, have not been uniformly successful in preventing re-cracking.

Weld overlays and thermal sprayed coatings have both been used successfully to control cracking. Weld overlays — primarily Inconel 72® and Type 309L stainless steel — have been applied in bands over structural welds to isolate

them from contact with cooking liquor. The overlay bands are themselves resistant to corrosion damage, but there have been instances of cracking of the carbon steel substrate in the heat-affected zone at the edge of the overlay band. Experience with thermal sprayed coatings has been limited, but it appears that flame-sprayed and plasma-sprayed stainless steel coatings protect underlying welds, provided the coating is sealed with a silicone-modified furan after application (25).

Anodic protection has been effective in controlling both corrosion and caustic cracking in several continuous digesters (26). Protection is achieved by passing a controlled DC current through an electrolytic cell consisting of the digester wall, the cooking liquor, and a special cathode installed inside the digester. A current of 1000A (at 12VDC) is required to passivate the vessel initially, but only a few hundred watts of electrical power will maintain anodic protection. The digester potential is maintained approximately 100 mV above the upper limit of the potential range required for cracking. Anodic protection has suppressed further cracking in several digesters previously susceptible to severe and chronic cracking.

Liquor Reheater Tubing. Corrosion and cracking have been encountered in stainless steel tubes in shell-and-tube heat exchangers used to heat circulating liquors. An example of a cracked liquor reheater tube is shown in Figure 7. In most cases, severe transgranular cracking occurs when liquor leaks onto the steam side of the tubes, where it is concentrated and heated by the steam. Caustic cracking and chloride stress corrosion cracking have both been implicated. Differential thermal expansion between the stainless steel tube bundle and the carbon steel shell apparently provides the stress required for cracking. Cracking has been eliminated in more than 100 kraft mills by the use

of a duplex stainless steel (3RE60) in liquor heater tubes; Inconel heater tubes have also been used successfully (27-28).

Corrosion of stainless steel liquor heater tubing is more puzzling, since stainless steel is generally resistant to attack by kraft liquors at liquor heater temperatures. Corrosion of liquor heater tubes may actually result from improper acid cleaning — e.g., using excessive temperatures or uninhibited hydrochloric acid.

### III. CORROSION IN RECAUSTICIZING EQUIPMENT

The recausticizing plant provides a variety of corrosive media, including white and green liquor, lime mud slurries, lime mud wash waters, and lime kiln scrubber waters. White and green liquors attack storage tanks, clarifiers, and piping fabricated from plain carbon steel but have little effect on stainless steel equipment (in the absence of abrasion). Erosion-corrosion is frequently seen on equipment in contact with abrasive lime mud slurries, such as clarifier rakes, lime mud slurry pump casings and impellers (e.g., Figure 8), and lime mud discharge lines. Corrosion also occurs on lime kiln scrubber components.

Plain carbon steel storage tanks and clarifiers in white and green liquor service suffer severe corrosive attack, particularly in zones where liquor levels fluctuate frequently. Figure 9 shows the variation in corrosion rate at different elevations along the sidewall of a white liquor clarifier (29). In the zone immediately above the outlet bustle pipe, the corrosion rate approaches 30 mils per year. Areas which are seldom immersed experience a much lower rate of corrosion, as do surfaces near the bottom which are protected by a layer of lime mud sediment. In multitray clarifiers, the trays experience a similar form of

attack. Little corrosion is seen on the top of the tray where lime mud settles, but severe attack occurs on the underside of the tray where air bubbles entrained in the liquor remain in contact with the tray. White liquor clarifiers and storage tanks often need extensive repair or replacement after only ten years of service, and instances of severe corrosion in less than two years have been reported.

The corrosivity of white liquor is strongly influenced by the liquor composition. In simulated white liquors containing only the important pulping chemicals, NaOH and Na<sub>2</sub>S, the rate of corrosion of carbon steel is less than 10 mils per year (30). However, the presence of thiosulfates and low concentrations of polysulfide in white liquor can increase the corrosion rate to more than 50 mils per year, as shown for thiosulfate in Table 2 (31). The effect of thiosulfate and polysulfide is greater in liquors containing high concentrations of NaOH and Na<sub>2</sub>S. The other species typically found in white liquor — sulfates, sulfites, chlorides, and carbonates — are apparently innocuous (31).

Since the hydrosulfide in white liquor is rapidly converted to thiosulfate by air contact, the high rate of corrosion at air/liquor interfaces is probably related to the thiosulfate effect shown in Table 2.

Liquor velocity relative to steel surfaces can also have a large effect on the rate of corrosion (32). As shown in Table 3, the rate of corrosion of carbon steel by white liquor is increased five-fold by a change from stagnant to laminar flow conditions. Under turbulent flow conditions, corrosion rates exceeding 150 mpy are possible.

Several corrosion control measures have been effective in recausticizing applications, including stainless steel fabrication, specification of thick-wall carbon steel at critical sites, controlling thiosulfate and polysulfide levels, the use of barrier linings, and anodic protection.

Type 304L stainless steel is not affected by white or green liquor, and stainless steel recausticizing equipment will probably last for the life of the mill. The higher cost of stainless steel can be mitigated to some extent by eliminating the corrosion allowance on wall thickness. There is little justification for using more costly Type 316L stainless steel in recausticizing applications; the high pH of the liquors inhibits chloride attack and precludes the need for molybdenum in the stainless steel. In vessels with corrosion at the liquid level line as shown in Figure 9, stainless steel "belly bands" can be installed to prolong tank lifetime. Usually, formed stainless steel plates are seal-welded to the inside wall. Careful installation is required to prevent liquor from leaking between the stainless cladding and the wall and accelerating wall corrosion.

Experience with alkali-resistant concrete and brickwork linings in recausticizing vessels has been checkered. In some cases, the lining prevents further corrosion damage. In many cases, liquor penetrates behind the barrier linings, allowing renewed attack of the wall. Installation of a protective polymeric membrane between the vessel wall and the lining may eliminate damage if the lining is breached.

Thiosulfate levels can be reduced by minimizing air contact with liquor, in order to lower corrosion rates in white and green liquor systems. Thiosulfates are formed wherever dissolved sulfides in the liquors come in contact with air.

Likely sites for thiosulfate formation include shatter jets (where smelt is dispersed as it falls into the dissolving tank liquor), splitter box weirs, storage tank and clarifier liquid surfaces, and leaking pump seals. Steam shatter jets are preferred over compressed air jets for reducing thiosulfate levels. In some cases, thiosulfates are generated when weak wash liquor is used to scrub lime kiln flue gases before being used as dissolving tank make-up liquor. Scrubber waters should be completely oxidized to convert thiosulfates to innocuous sulfates before use as dissolving tank make-up liquor.

Natural polysulfide levels are negligible in most white liquors. However, polysulfide-accelerated attack can occur if emulsified sulfur is added (for sulfur make-up) in the recausticizing plant, since elemental sulfur is rapidly converted to polysulfide. Make-up sulfur should instead be added to black liquor, where corrosion consequences are minimized.

Recently, anodic protection has been shown to be an effective and economical corrosion control measure for use in white liquor storage tanks and clarifiers (29). In a prototype installation on an operating clarifier with severe corrosion damage, corrosion rates were reduced by nearly an order of magnitude by holding the rest potential of the vessel in the passive range. The anodic protection system is shown schematically in Figure 10. Although relatively large currents were required to achieve initial protection, little power is needed to maintain protective passivation.

Erosion-corrosion is a severe problem wherever abrasive lime mud is found. Stainless steel fabrication is appropriate wherever abrasive conditions prevail, as in rakes and rake arms in white and green liquor clarifiers. In severely abrasive conditions, such as lime mud pump impellers, hard-facing overlays such



as Stellite® may be effective, but periodic replacement of components is usually necessary.

#### IV. CORROSION IN BLACK LIQUOR PROCESSING EQUIPMENT

Black liquor varies considerably, depending on the pulping process used, the pulping yield, and the stage of chemical recovery. Weak black liquor, the filtrate obtained from brown stock washing, contains approximately 20% solids consisting of organic compounds extracted from the wood (principally lignin compounds), inorganic salts not consumed in the pulping process, organic acids, and various hemicelluloses and sugars. The pH of weak black liquor is on the order of 12, and the residual active alkali (NaOH and Na<sub>2</sub>S) can range from 4 to 30 g/L. The solids content of heavy black liquor is increased by evaporation into the 60-75% range, and heavy black liquor at room temperature is viscous and semisolid. Black liquor oxidation may be used to convert reduced sulfur compounds in black liquor to thiosulfates and sulfates, in order to reduce odorous emissions from the recovery boiler and to conserve sulfur in the process.

Corrosion of brown stock washing equipment is rarely a concern in the kraft pulp mill. Brown stock washing is usually carried out on rotary drum vacuum washers, although displacement washing is becoming more common. Washer drums are usually fabricated from carbon steel, while backing wires and face wires are usually stainless steel. The moderately high pH of weak wash filtrate, together with the low concentration of NaOH and the inhibitive effect of the dissolved organic species, generally prevent severe corrosion of brown stock washing equipment, in spite of the dissimilar metal construction. However, corrosion can become a problem if the pH of the weak wash filtrate is depressed by use of acidic bleach plant filtrate as shower water, or by addition of neutral sulfite

semichemical pulping liquors. When acidic filtrates are used, it is common practice to raise the pH above 10 to reduce corrosion and to prevent odorous emission of hydrogen sulfide gas.

The details of black liquor evaporation equipment vary from mill to mill. Multiple effect evaporators are generally used to increase the black liquor solids to the 55% level, while concentrators or cascade evaporators complete the evaporation. The shell and tube heat exchanger (rising film, long tube vertical evaporators) is the most common evaporator design, but other configurations with plates and falling films are becoming more popular. Plain carbon steel and Types 304L and 316L stainless steels are common materials of construction. Stainless steel tubes are used in the higher temperature evaporator effects ( $> 200^{\circ}\text{F}$ ); both stainless and carbon steel tubes are used at lower temperatures. Black liquor storage tanks are usually made of plain carbon steel, as is most black liquor oxidation equipment. Stainless steel piping is commonly used for black liquor transport.

Generally speaking, black liquor is much less corrosive toward carbon steel than the recausticizing liquors, since the concentrations of NaOH and  $\text{Na}_2\text{S}$  in black liquor have been reduced by the pulping reactions. The residual alkali in black liquor maintains the pH near 12, which stabilizes a protective film on the steel surfaces. In spite of this film, carbon steel storage tanks wetted by black liquor may experience pitting and crevice corrosion, particularly at the liquor level line and underneath sediments and scales. Pitting attack, such as that shown in Figure 11, is often encountered on roofs and other surfaces which are exposed to vapors emanating from the black liquor. This pitting is attributed to volatile organic acids that condense on cooler surfaces but are not neutralized by direct contact with the alkaline black liquor.

Remedial measures for corrosion in black liquor storage tanks are limited. Generally, the moderate rate of attack does not justify the use of stainless steel for tanks and vessels. Although the high temperatures and organic sulfur compounds in black liquor make FRP generally unsuitable for immersion service, some mills have installed fiber-reinforced polymeric roofs on black liquor storage tanks to minimize pitting attack. Thick wall carbon steel construction and the use of stainless "belly bands" may also be beneficial when attack is restricted to one area, such as the liquor level line.

Stainless steels are generally resistant to corrosion by black liquors at temperatures normally encountered in evaporation and concentration equipment. Over the years, experience has shown which evaporator components must be stainless to prevent excessive corrosion, so severe evaporator corrosion is now relatively infrequent. Tubes, vapor deflectors, and liquor boxes are generally stainless steel or stainless-clad carbon steel, particularly in the high temperature effects. When localized corrosion does occur on carbon steel surfaces in modern evaporators, it can usually be traced to unanticipated contact between hot liquor and the steel due to foaming, excessive throughput, or other operating misadventures. In these cases, stainless steel weld overlays or thermal spray coating applied to the carbon steel surface usually forestall continued corrosion.

Although black liquor oxidation produces high levels of thiosulfate in the black liquor, the thiosulfates are much less injurious to carbon steel in black liquor service, compared to the recausticizing situation. Oxidized black liquors have low residual alkali levels because of consumption of NaOH in the digestion process and complete oxidation of Na<sub>2</sub>S. In the absence of significant concentrations of NaOH and Na<sub>2</sub>S, thiosulfates are relatively innocuous toward

carbon steel. Consequently, it is desirable to oxidize weak black liquor, rather than strong black liquor, so that more of the black liquor process equipment benefits from the reduced corrosion that accompanies black liquor oxidation. Carbon steel is generally adequate for oxidation equipment and oxidized black liquor storage.

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## FIGURES

- Figure 1. Schematic representation of kraft pulping and chemical recovery.
- Figure 2. Erosion-corrosion of a blow target plate by pulp discharged at high velocities from a batch digester.
- Figure 3. Macrograph showing cracking in a sample taken from a continuous digester weld.
- Figure 4. Photomicrograph showing branched, intergranular nature of cracking in an actual continuous digester weld.
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Table 1. Recommended Weld Overlay Composition for Batch Digester Protection (19).

Alloying Element	Weight, %
Carbon	0.15 max.
Manganese	2.50 max.
Phosphorous	0.045 max.
Sulfur	0.030 max.
Silicon	1.00 max.
Chromium	18.0 min.
Nickel	8.0 min.
Molybdenum, when desired	Cr:Mo>=8:1

Table 2. Effect of Thiosulfate Concentration on White Liquor Corrosivity (8-week exposures).

NaOH (g/L)	Na <sub>2</sub> S (g/L)	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> (g/L)	Corrosion Rate (mpy)
80	20	0	7
80	20	2.5	7
80	20	10	11
80	20	25	28
80	20	50	53
80	40	2.5	6
80	40	5	20
80	40	10	21
80	40	25	43
80	40	50	87



Table 3. Effect of Liquor Velocity on White Liquor Corrosivity of Simulated Liquor, 100 g/L NaOH + 33 g/L Na<sub>2</sub>S.

Velocity (m/s)	Corrosion Rate (mpy)
0.0	5
0.14	65
0.25	80
0.30	99
0.43	120
0.50	143
0.86	138
1.32	150
2.62	148



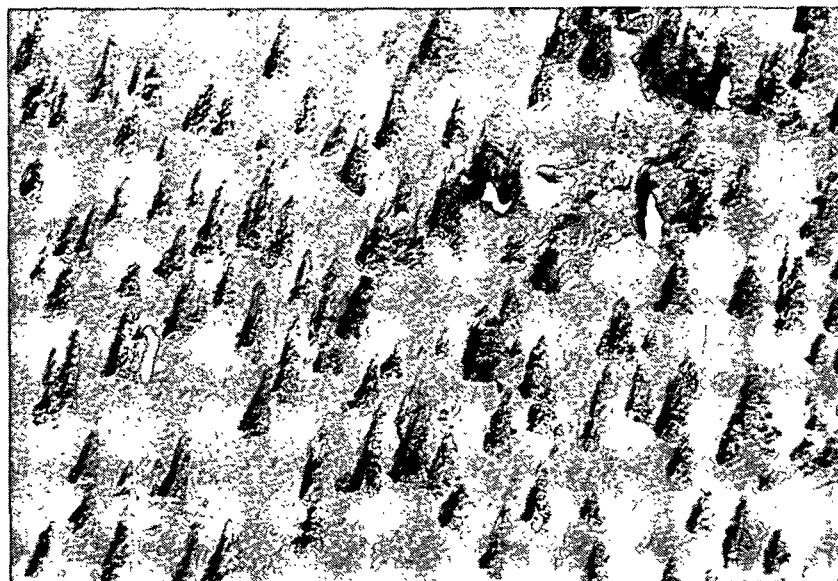


Figure 2. Erosion-corrosion of a blow target plate by pulp discharged at high velocities from a batch digester.

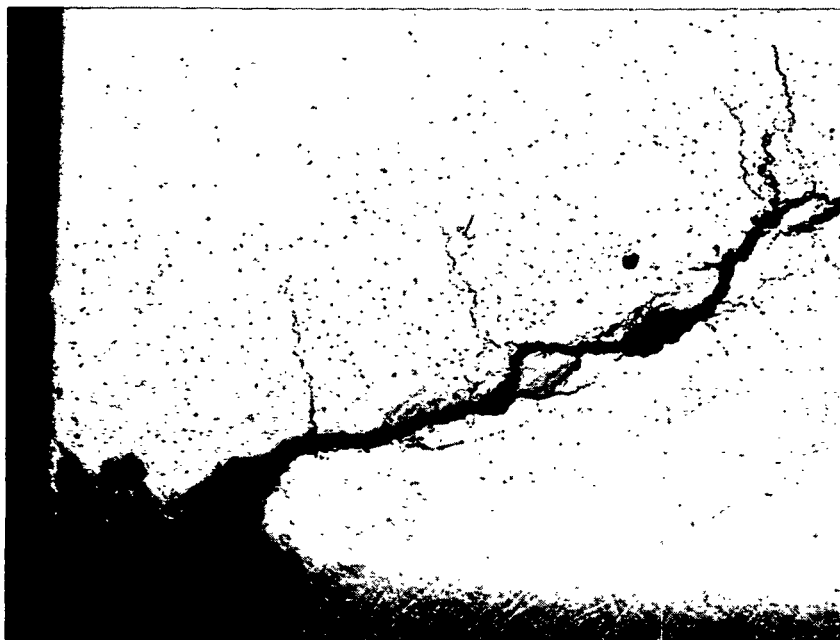


Figure 3. Macrograph showing cracking in a sample taken from a continuous digester weld.

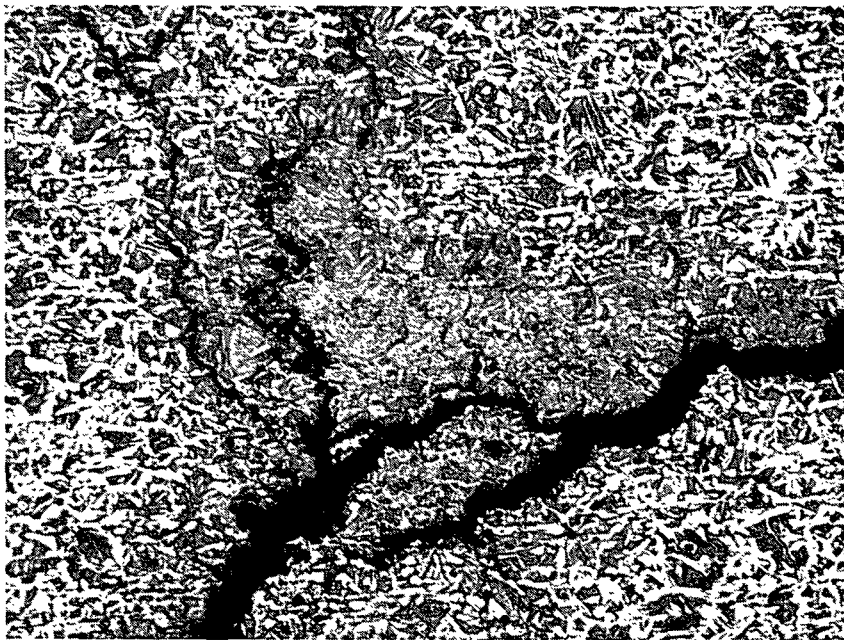


Figure 4. Photomicrograph showing branched, intergranular nature of cracking in an actual continuous digester weld.

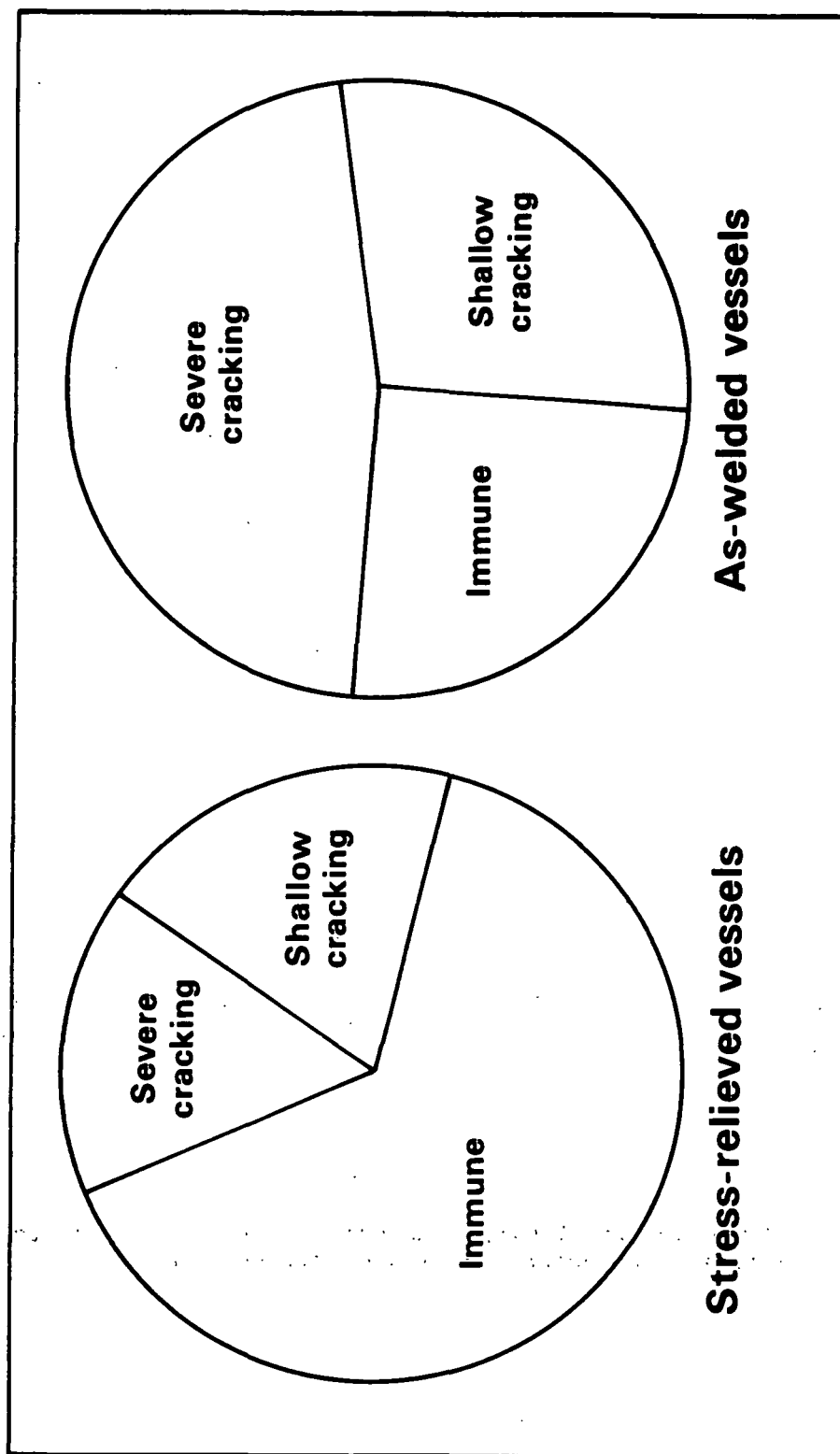


Figure 5. Effect of stress relief on stress corrosion cracking susceptibility of continuous digesters.

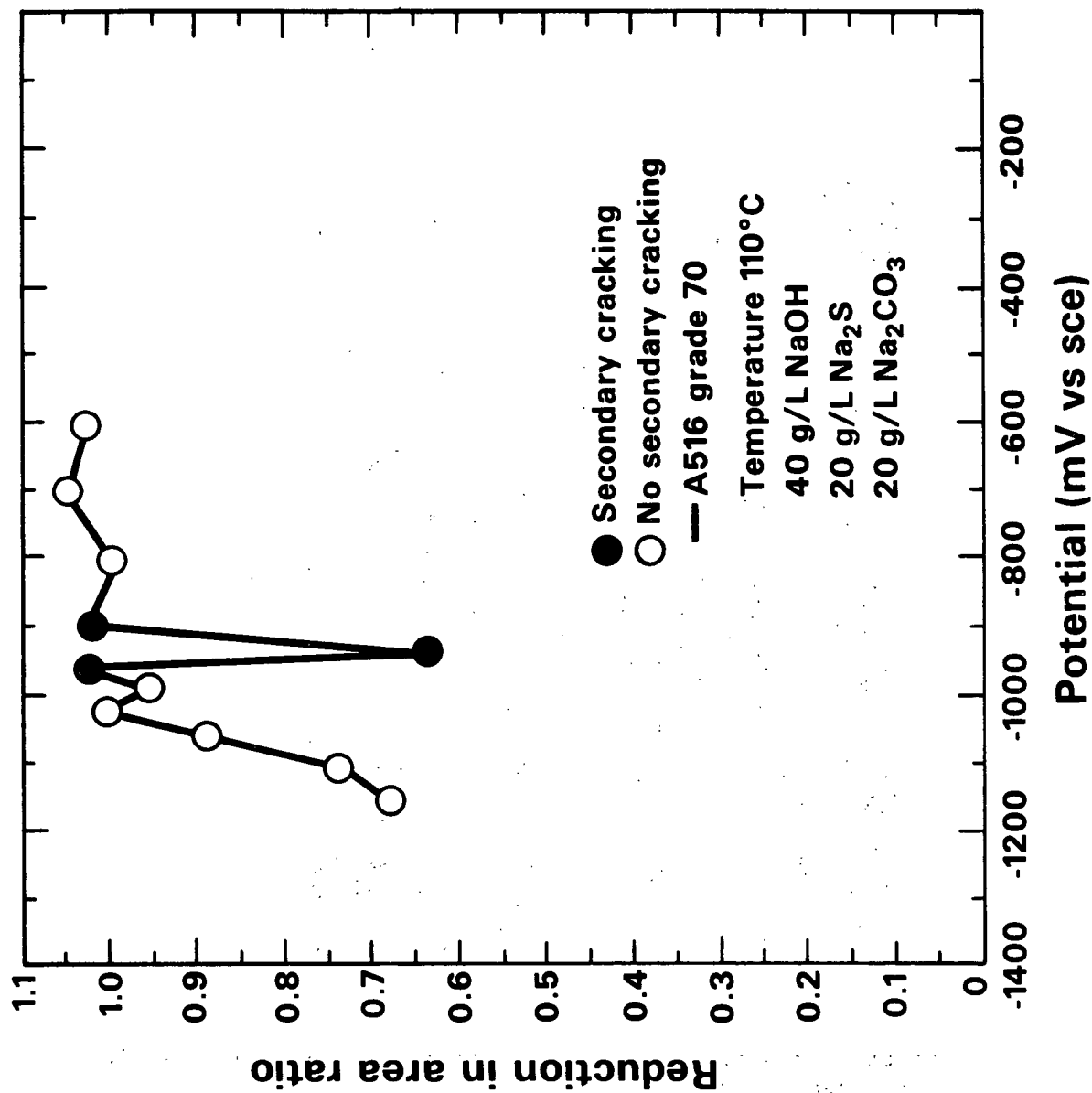


Figure 6. Plot showing the effect of potential on cracking severity in controlled-potential slow strain rate testing of digester steels exposed to a simulated impregnation zone liquor.



Figure 7. Transgranular stress corrosion cracking of Type 304L stainless liquor reheater tubing.



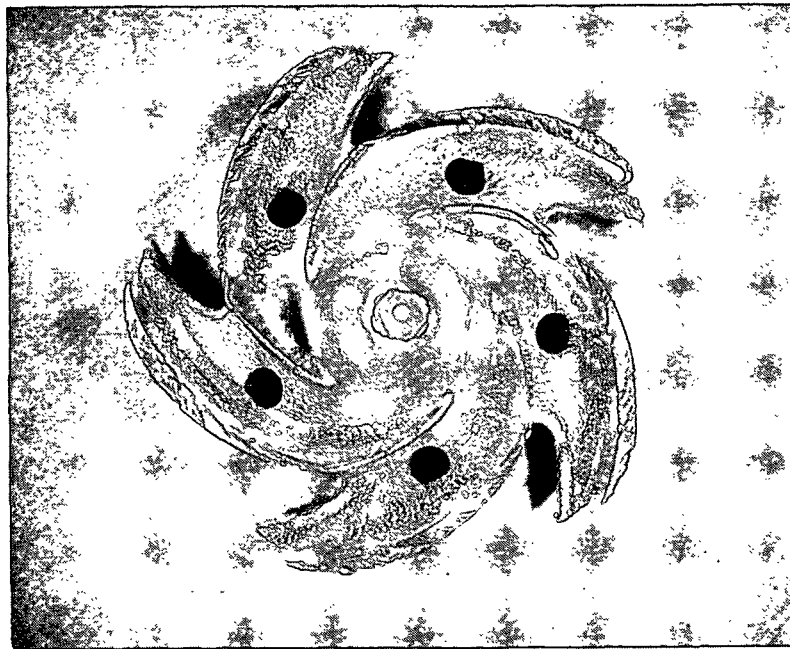


Figure 8. Erosion-corrosion of a lime mud pump impeller.

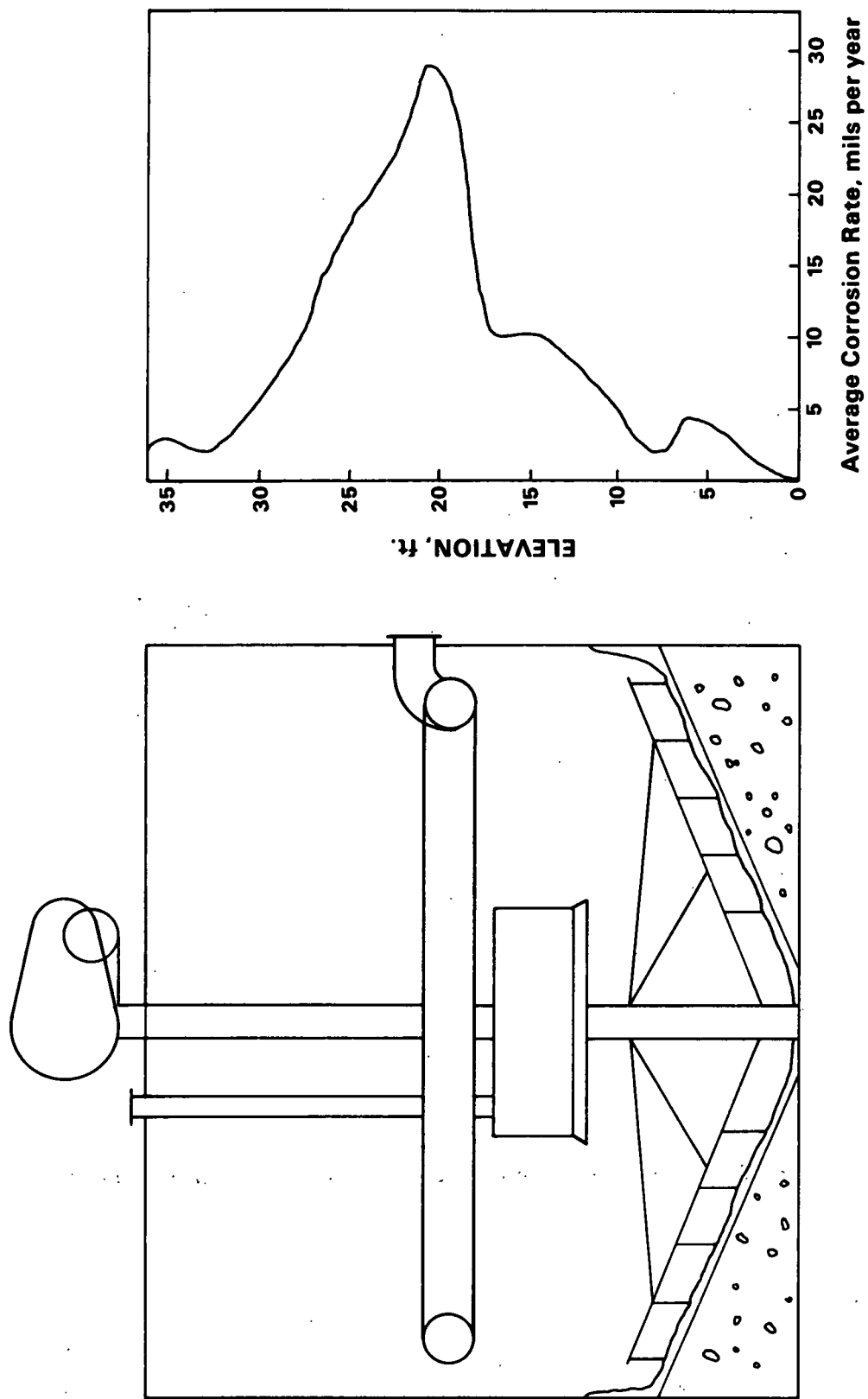


Figure 9. Variation of corrosion rate with elevation at the wall of a white liquor clarifier.

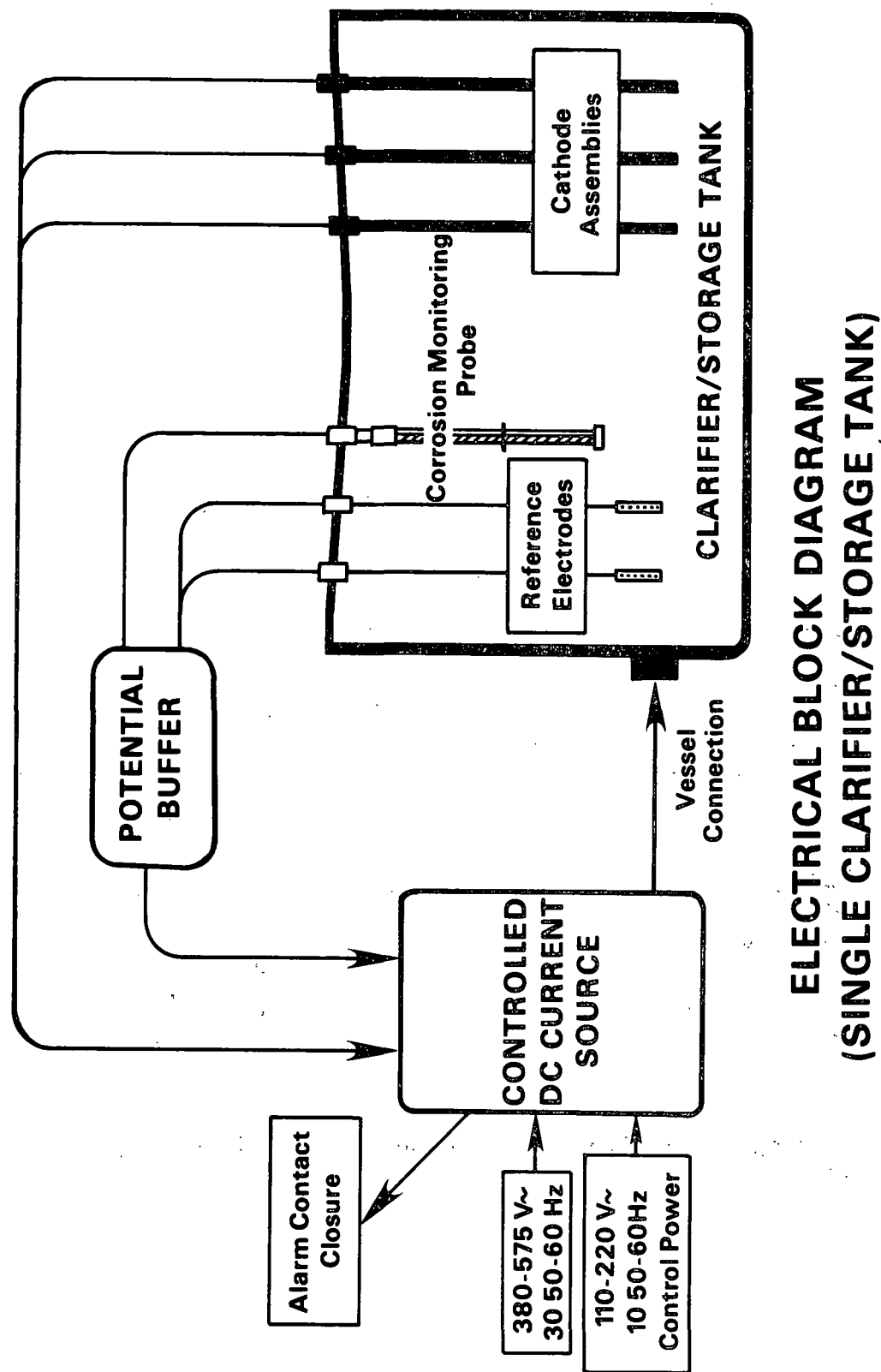


Figure 10. Schematic diagram of an anodic protection system for recausticizing storage tanks and unit clarifiers.

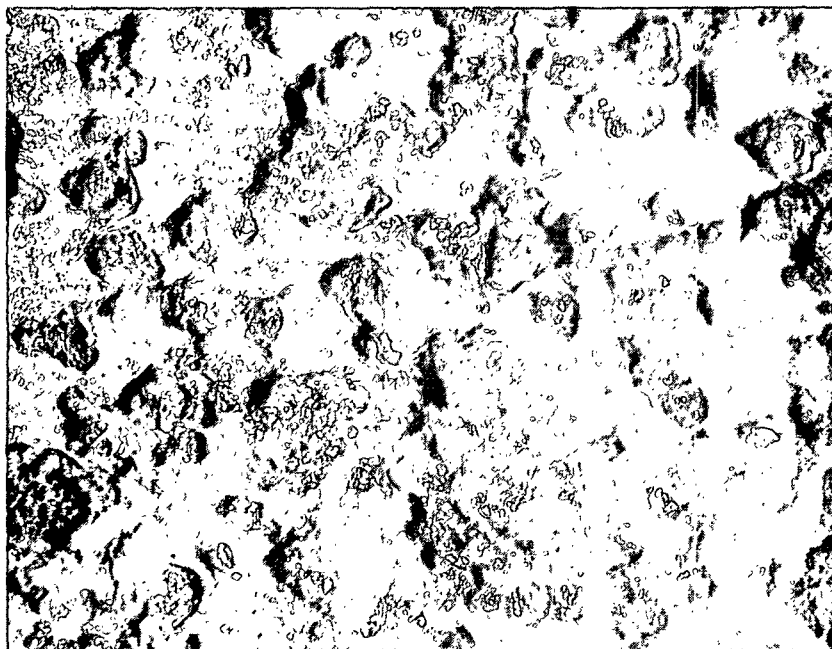


Figure 11. Pitting of a carbon steel root section in a black liquor storage tank.